

Study of Zn–Sn–Al Solder Alloys

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Submitted by

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CERTIFICATE



This is to certify that Mr. SANJEEB KUMAR SINGH (110MM0384) and Mr. RAJAT BHENGRAJ (110MM0489) have carried out their project on the topic entitled “Study of Zn-Sn-Al solder alloys” under my supervision for the award of the degree of bachelor of technology. This part of the work has not been submitted to any other institute for any degree or diploma. The work contained in this thesis is original and has been done under my supervision.

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1. ABSTRACT

In the electronic industry Pb-Sn solder is a very important material but Pb is toxic and has adverse effects on the environment and human beings. Due to the harmful effects of the Pb the use of the Pb-Sn solder alloys are being avoided and new Pb-free solder alloys are being used for electronic applications. The Sn – Zn – Al alloys are one of significant candidates in the proposal of alternative lead-free solders for high temperature soldering. Three Sn – Zn – Al alloys were prepared and studied experimentally. The micro-hardness and X-ray micro-analysis of the samples were conducted. The specimens were studied metallographically including SEM (BSE) in order to determine the composition and identification of individual phases. Melting point and significant temperatures of the alloys are found by DSC and TGA analysis. The diagram of the Al – Sn – Zn ternary system is given thermodynamically more precisely on the basis of our complex study. The fracture analysis was also done with the help of FESEM. The basic difference between the eutectic solder and addition of Aluminum was observed. Economics of the processing of the solder was briefly discussed.

2. INTRODUCTION

In today's world, Electronics and its production is quite an important phenomenon. Every gadget that we use in our day –to-day lives is attributed to the world of Electronics. The manufacture of electronic circuits and equipment is quite dependent on the process of Soldering.

Soldering is the method of producing coalescence of materials by heating to a temperature ($<450^{\circ}\text{C}$) i.e below the solidus of the base metal in presence of filler metal. Instead of forming and adhesive bond solder forms a different alloy by chemical reaction. Some of the advantages include choice of temporary or permanent joint, joining of dissimilar metals, and flexibility in rate of cooling and heating and easy realignment. Full application of lead free solders in industries such as automobiles remains a challenge till date. Lead-free solders of various compositions are used. They are able to substitute the lead based solders in specific applications, but the electronic industry is not satisfied because the lead-free solders often have reliability problems, usually caused by worse mechanical properties, and/or higher tendency to oxidation, higher occurrence of 10 undesirable intermetallic phases, higher melting temperature. They are also generally more expensive (for example Sn–Ag based solders) or their usage leads to higher technology expenses. Systems on the Al–Zn base with another alloying element, such as Ga, Ni, Sn, seem to be promising candidates taking also into account that some of the elements represent substrate materials.

We synthesized an optimum-temperature solder with a melting point of 199°C by incorporating aluminum (Al) to Sn-Zn-based material to enhance corrosion resistance and help reduce its oxidization.

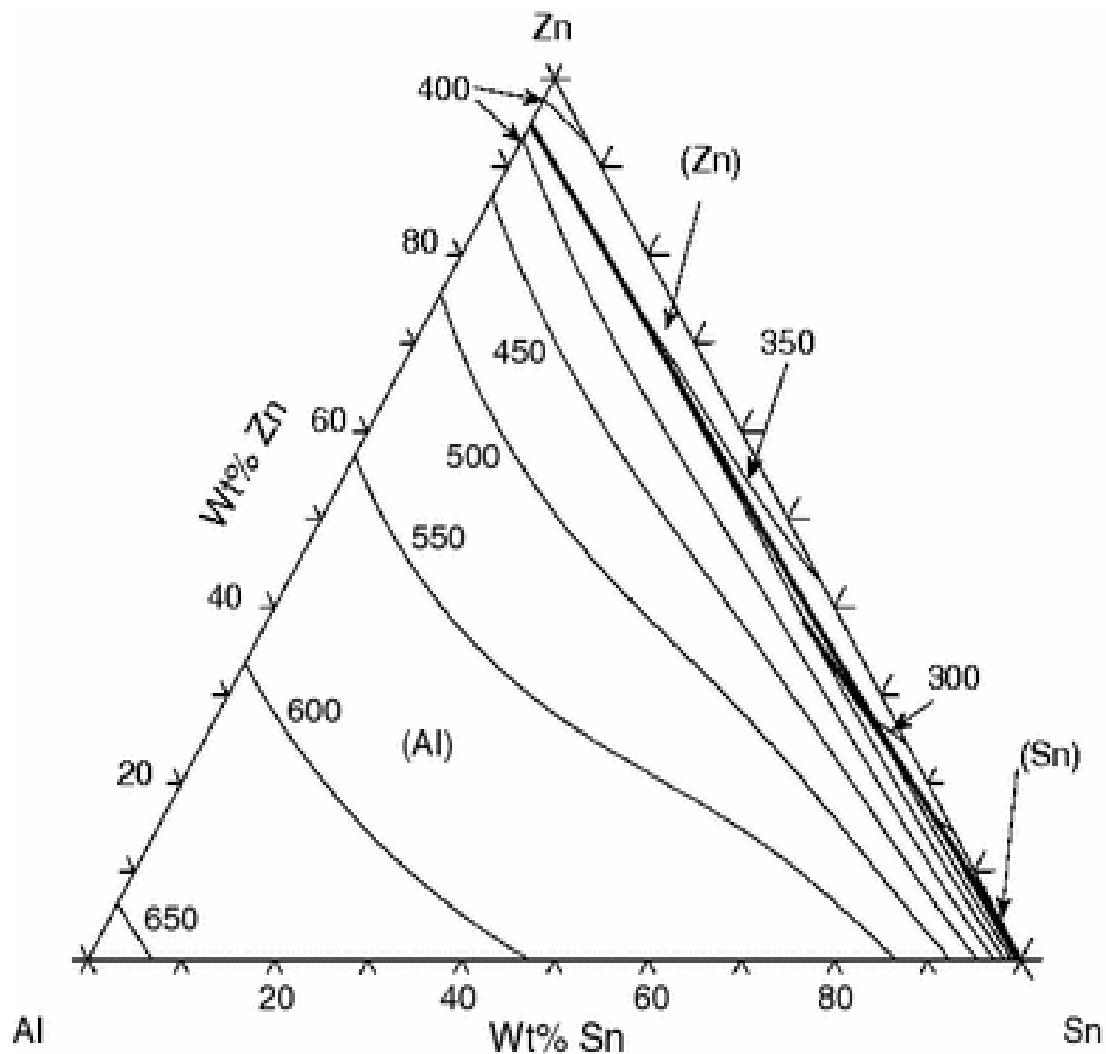
The specimens prepared experimentally are evaluated from the viewpoint of physical, chemical, structural, mechanical, technological and usable properties. The achieved findings are confronted with thermodynamic calculations of ternary systems

3. LITERATURE SURVEY

3.1 Binary & Ternary Systems

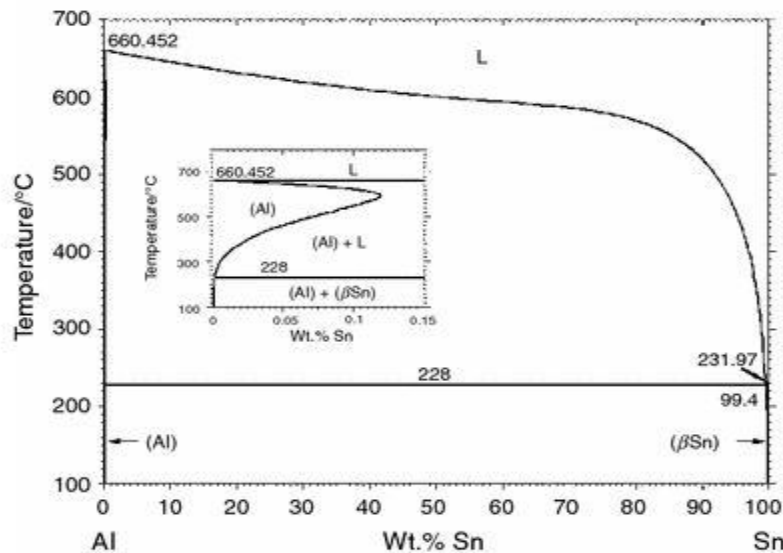
3.1.1 Al – Sn – Zn ternary system

The diagram of the Al – Sn – Zn ternary system was published in various journals. Thermal analysis of ninety three alloys, prepared by melting, 99.995% Al, and 99.933% Sn and 99.99% Zn in an argon atmosphere was performed by Prowans et al. The solidus and liquidus surfaces as well as three vertical sections were determined. The ternary eutectic composition was determined by zone melting. Using various experimental data, [5] a complete set of thermodynamic functions of all the phases were derived.



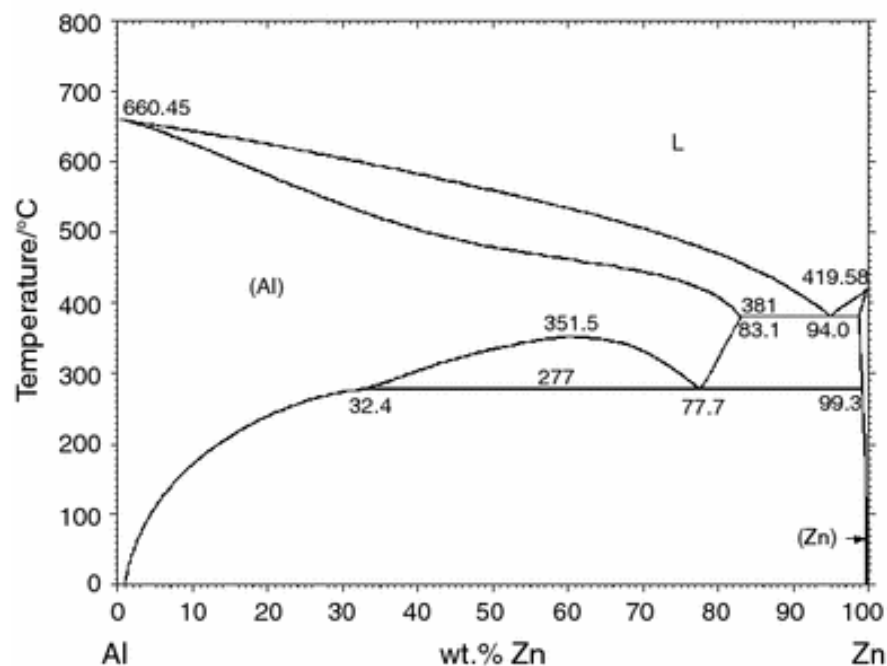
3.1.2 Al – Sn binary System

The Al-Sn binary system is of the simple eutectic type. The eutectic reaction takes place at the temperature of 228.5°C in the alloy containing 97.6 % Sn.



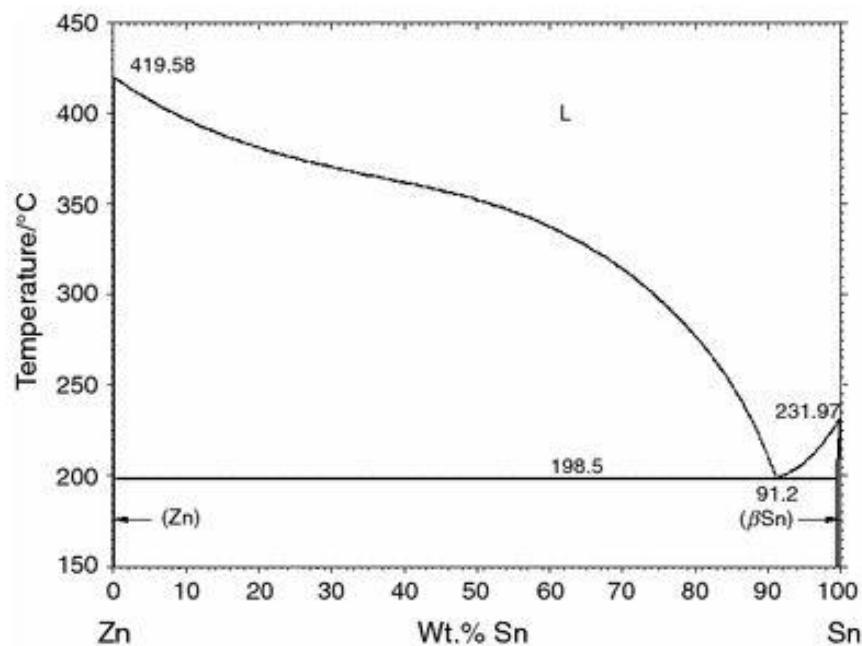
3.1.3 Al – Zn binary System

The equilibrium phase Diagram of Al-Zn is a eutectic system involving a monotectoid reaction. The eutectic reaction proceeds at 381°C close to the Zinc side (eutectic point has 88.7 % Zinc). The monotectoid reaction occurs at the temperature of 277 °C.



3.1.4 Zn – Sn binary System

The Zn-Sn binary system is a simple eutectic system. The eutectic reaction takes place at the temperature of 198.5°C in the alloy containing 85.1 % Sn.



3.2 Harmful effects of lead on human life

According to the Environment Protection Agency (EPA), Lead and its compounds are one of the top 17 chemicals posing the greatest threat to human life. When lead comes in contact with human body over a period of time, it bonds with proteins in the body and slows down their usual functions. If the amount of lead in the blood cells is greater than normal concentration, lead poisoning occurs. When considering the case of hand operations of soldering, Pb contamination is not a huge problem as at normal soldering temperature, lead is less nonvolatile.

However the ingestion of Lead vapour and Lead dust formed during wave soldering operation can have hazardous effects on our health. During wave soldering operation, the formation of dross is normal due to oxidation at the surface of molten solder. The interesting fact is that 90% of the dross which is produced can be refined for reuse but the remaining 10% is of no use. The Resource Conservation and Recovery Act (USA) has specified that this waste is dangerous to human health, classified and proper care and disposal of this waste has to be carried out.

3.3 Lead poisoning

Lead Poisoning is also called Plumbism. Lead is of no biological advantages to human beings. Lead affects the metabolism of Calcium and vitamin D. Lead toxicity interferes with a large number of body functions and many organs which comprise of heart, kidney, intestine and nervous system. It slows down the development of nervous system and therefore is more dangerous to children. The lead paint used in houses is also harmful. So children are more affected by lead poisoning than adults. It has been observed that increased blood lead level in children associated with decrement in intelligence, memory, and attention, reading and arithmetic ability. The amount of lead, in the blood cells, determines lead toxicity. The US centers for disease control and prevention and the World Health Organization (WHO) states that if lead level in blood is greater than 10 µg/dl, it may slow down tissue level

3.4 Sources of exposure

Industrial use of Lead (Pb-acid batteries, Pb wire or pipes and electronic components), metal recycling and foundries constitute the important routes of Lead poisoning. Lead exposure may also be caused from contaminated water through lead pipes, soil and air. There are various ways of contamination of lead in solid which comprises of residues from lead containing gasoline, pesticides, used engine oil, waste landfills or from industries like smelter plants. Water supply pipes, made up of lead or repaired by lead solder joints; possess a high level of danger to human life. The level of lead dissolved in water relies on the acidic nature, temperature, water hardness and standing time of water. It has been found that, in the US, 14-20 % of total lead poisoning is caused because of drinking water. In 2004 one article from “The Washington Post” published about the lead concentration in the drinking water and was awarded for this work. How lead toxicity affects human health?

After being absorbed, lead easily bonds with the proteins and enzymes present in the human body. It travels along with the blood and majorly attacks the soft tissues in the body. After many days, most of the Pb move to the teeth and bone marrow. In adults 94 % of the total lead concentration is confined in the bone and teeth while in case of children 73 % of the total lead content of the body is stored in the bone marrow.

(a)Renal system

Kidney Failure may be caused by higher level of lead in human blood cells. It can also cause fanconi syndrome which ceases the normal function of kidneys.

(b)Cardiovascular failure

Evidences have been found that lead exposure may cause heart rate variability high blood pressure, coronary heart disease and heart attack.

(c)Reproductive system

Both male and female reproductive systems are affected by lead poisoning. In the case of men, where the concentration of lead exceeds 40 $\mu\text{g/dl}$, sperm count decreases drastically. It is more dangerous in case of pregnant women as the elevated blood lead level may lead to miscarriage, prematurity and moreover may be harmful to the child .

(d)Nervous system

The axons of nerve cells degenerate and lose their usual function pertaining to response to the stimuli because of the lead poisoning. Our brain is the most sensitive organ and it is covered by endothelial cells. These cells act as a barrier between our blood and brain cells. Lead passes through this layer because it can resemble calcium ions. In the developing brain of a child, lead slows down the formation of synapse in the cerebral cortex, neurochemical development and network of ion channels. It decreases numbers of neurons, affects neurotransmission and reduces neuronal growth.

3.5 Lead's effect in environment and other species

The waste disposal of electrical and electronic assemblies containing lead and its compounds are considered dangerous to the environment. The lead containing components are dumped in solid waste landfills. These waste components contaminate ground water. The usual purification process is not applicable for removal of lead. Technically it is quite difficult to explain how lead forms bond with water. However a study has shown that PbO converts to PbCO_3 in presence of CO_2 and Cl . In the world market, Japan and USA are regarded to be the two major suppliers and users of printed circuit board (PCB) assemblies. The current studies show that this market will get doubled in the next 10 years. Hence, the proper disposal of lead containing components is not a trivial issue and we cannot neglect it. Recycling of lead appears to be one of the major remedy to the above problem. However, the use of recycled lead is limited. It has been reported that the recycled lead displays higher α -particle emission than pure lead and it affects the performance of electronic circuits

The lead level in our environment is not constant. It is increasing rapidly due to rapid industrialization during last few years. Lead content of 0.003 mg/l of water is regarded normal and nonhazardous to our ecosystem. In India several rivers have been found to be contaminated with high amounts of lead. The famous Hussain Sagar lake water is probably contaminated by the industrial waste of the city. During ‘GreenRevolution’, the greater consumption of lead containing pesticides in Punjab and Haryana has resulted in soil and water contamination up to a high level. Lead, in the form of soluble water sample was tested and found to be highly contaminated by lead. This and insoluble organic salts, is present in the soil. Plants usually absorb them through roots. Among plants, Lead toxicity depends upon its absorption, transport and intracellular localization. It has been observed that the plants growing in urban areas are more prone to lead poisoning. Lead reacts with some relevant functional groups of enzymes and slows down their normal operation, some of which helps in photosynthesis and nitrogen assimilation. However lead toxicity is not extreme in presence of organic and inorganic salts consisting of potassium and phosphates in a few cases

Several tests have been carried on plants and other animals. These test results show that lead poisoning also affects animals. The symptoms are similar to that of human race like abdominal pain, peripheral neuropathy and behavioral changes. The hunters

usually use lead bullets for hunting wild animals. The predators that eat those hunted animals are also affected. In many countries like the USA and Canada, lead-containing bullets have been banned. Turkey vultures and California condors, the two critically endangered species are also affected by lead poisoning when they feed on dead bodies of animal shot with lead bullets.

Accidental cases:-

On October 5, 2010, in Nigeria, at least 400 children died from lead poisoning (Zamafara state lead poisoning epidemic). More than 1000 children from 10 different villages residing near Yuguang gold and lead smelter plant in China were reported to have excess blood lead level.

After this incident, about 15000 people from that area relocated to other places. The Government has ceased the production of lead from 32 lead plants.

3.6 Legislation:-

On Friday October 11, 2002 European Community Members (currently France, Germany, Italy, Austria, Denmark, Belgium, Finland, Spain, Portugal, Sweden, Greece, Holland and the UK) banned the use of some dangerous substances in electrical and electronics equipments. It has been decided that four heavy metals (lead, cadmium, mercury and hexavalent chromium) will not be used further from 1 January 2004. In the US, laws have been introduced regarding elimination of Pb. In Japan, the use of lead has not been banned yet. However their laws prohibit lead from being sent to the landfills and other waste disposal

yards. Many of the Japanese companies have commenced to act to this and set their own methodologies for manufacturing lead free equipments. Seiko Epson Corporation stopped using lead bearing solders in PCBs and other components since March 2002. In India there is no such law prohibiting the usage of lead and its components. Despite various adverse health effects caused by lead, it is still widely used in consumer products. But the toxicity and threatening effects of lead on human health should not be neglected. In the near future, we may only have two options (a) 100% recycling of lead or (b) use of lead free equipments.

3.7 Role of Pb in Sn-Pb solder:-

Lead is relatively cheap and widely available. The soldering alloys which are based on eutectic or near the eutectic composition of Tin-Lead system and have been studied and redefined with many years of experiments by researchers. Sn-37Pb (eutectic composition) or Sn-40Pb is the mainly used solder in the electronic industries. The presence of lead has the following technical advantages:

- Lead acts as a solvent, allowing other metals such as Tin and Copper to form intermetallic via the process of diffusion.
- Lead prevents the transformation of white Tin to gray Tin upon cooling. This transformation, if occurred, results in an increase in volume and affects the structural integrity of Sn.
- Pb decreases the surface tension of pure Sn, which facilitates wetting.

The above three factors make lead the most suitable alloying agent for production of solder alloys.

3.8 Role of Tin:-

White Tin transforms into gray Tin if kept for a long time at a temperature below 0°C. In accordance with the thermodynamic data, the transformation temperature between the two phases is 13°C. It is quite to observe that a metal (white Sn) gets converted into a semiconductor (gray Sn) with an increase in volume (27 %). However a large increase in volume change fuels cracking in Sn microstructure. Tin easily wets the substrate and spreads on it. This makes tin a major constituent in most of the solder alloys. However, the above transformation gives rise to problem for devices that cycle across 13°C. Under the application of repeated thermal cycling, plastic deformation and crack formation are likely to occur even without any application of external load. In accordance with previous works Copper, Aluminum, Zinc and Germanium enhance the formation of gray Tin while lead, Antimony, Cadmium and Bismuth has a negative effect on this transformation (crystal growth appearing like fine wires) in Tin occurs rapidly at about 51°C. These whiskers are tetragonal white tin (β -tin) that grow because of internal stresses and

strains. Whiskers do not affect solder-ability but longer whiskers may cause short-circuits in printed circuit assemblies. It has been observed that addition of lead suppresses the whisker growth in tin.

3.9 Oxidation of Sn-Zinc-Al solder: theoretical discussion

The addition of Aluminum considerably improves the wettability of a Tin-Zinc solder. The appropriate reason for preferential oxidation of solder by Al over Zn is due to relative affinity towards oxygen molecules.

As Zinc absorbs oxygen on the surface and forms a Zinc oxide layer, it is not the end as oxygen molecules progressively enter the porous ZnO layer and increase the oxide layer thickness. So the wetting power of the solder decreases significantly. However, when Aluminum atoms are added in place of the Zinc, the Aluminum atoms come in contact with air, formation of a dense Al_2O_3 layer takes place. It is known that Aluminum atoms are prone to release electrons partially due to their chemical properties and react with oxygen molecules. Segregation of Al atoms in the solder prevents the contamination of Zn with oxygen. Electron releasing Al atoms are constantly provided to the metal surface as a state of interface is maintained between oxygen molecules and metal surface on positive and negative side respectively.

Furthermore, because an Al_2O_3 oxide film consisting of Aluminum restrains the entry of moisture, it improves corrosion resistance in a high temperature, high-humidity environment.

4. EXPERIMENTAL PROCEDURE

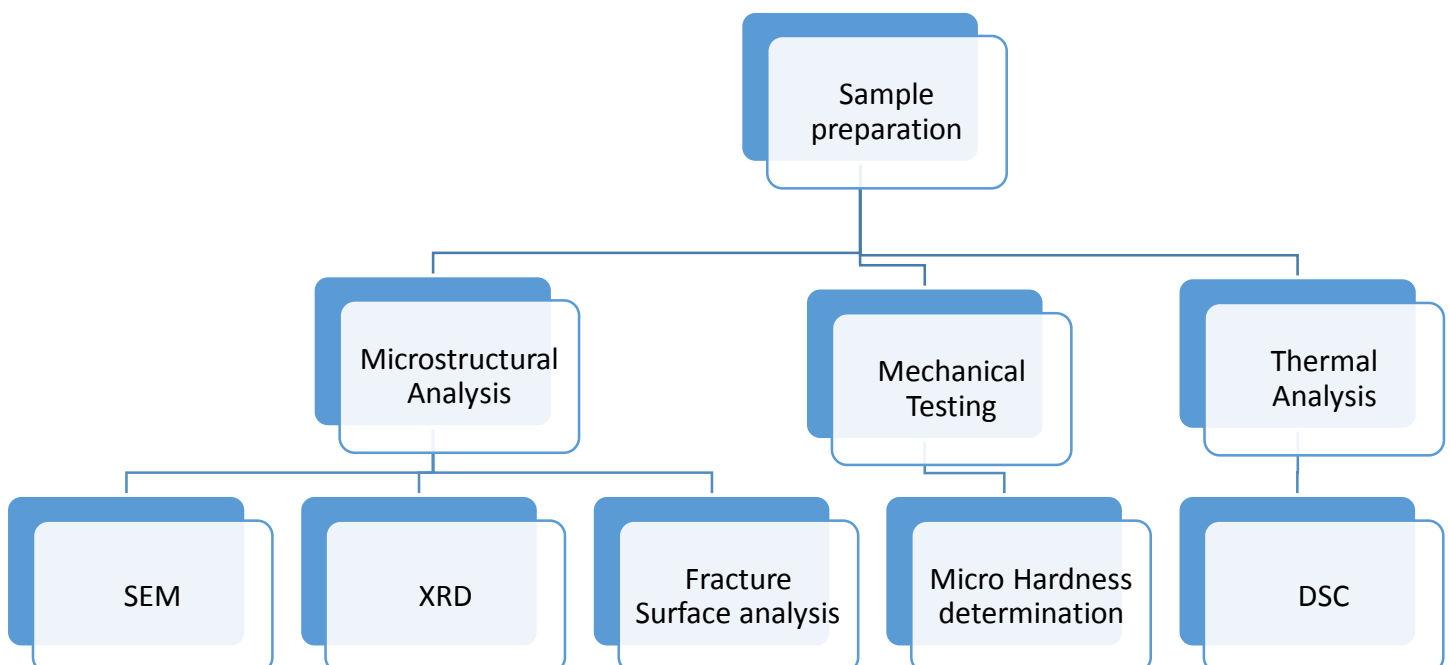
4.1 Materials and Method

We procured Al power, Sn granules, Zn foils and prepared three samples of composition as follows

Composition	Al (wt%)	Zn (wt%)	Sn (wt%)
Sample 1 (furnace cooled)	3	15	82
Sample 2 (furnace cooled)	7	43	50
Sample 3 (air cooled)	3	15	82

1. First we calculate and take materials according to the above composition (without the Al powder) and put it in a crucible.
2. Then we insert the crucible in a muffle furnace and heat it to required temperature (700°C) till complete melting occurs.
3. Then we take out the crucible and add Al powder and again reinsert the crucible into the furnace. The samples are kept at 700°C for 2 hours.
4. The sample which is to be furnace cooled is left in the furnace and the sample to be air cooled is kept outside.
5. After the sample is cooled the solder is removed carefully from the crucible

4.2 Flow-chart of the experimental procedure

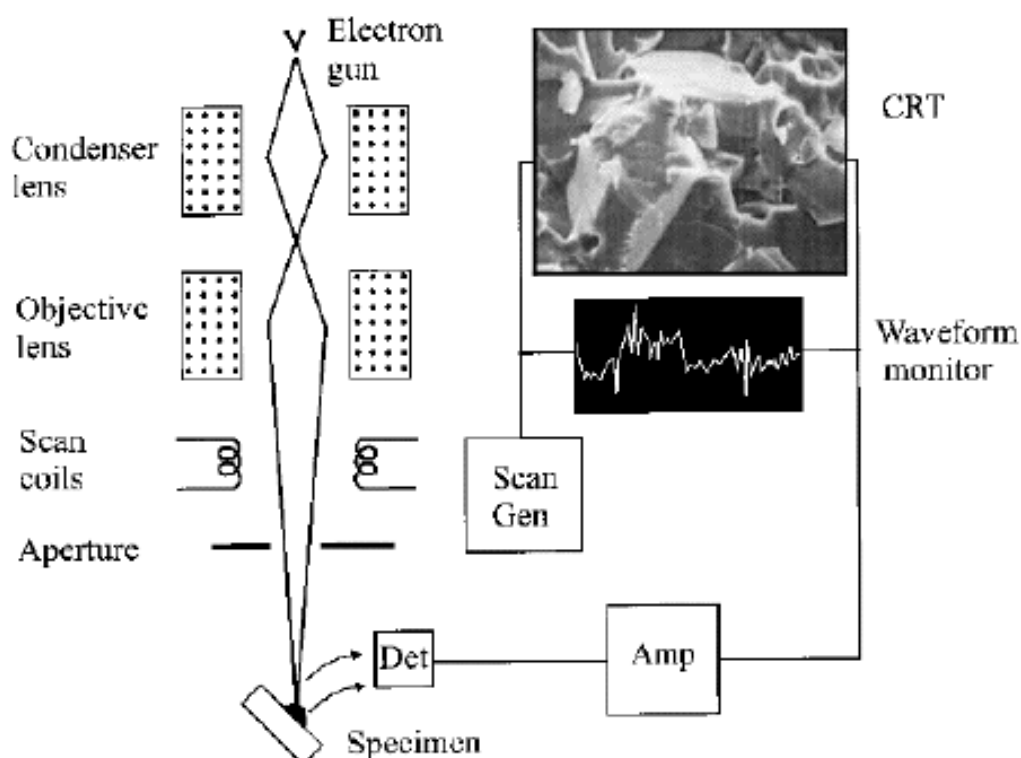


4.3 Experimental Instruments

4.3.1 Scanning Electron Microscopy:

Scanning electron microscope (SEM) is a variant of electron microscope that focusses a beam of high energy electrons on the sample and subsequently produces images. The resolution of the **SEM** is in the range of 10 nanometers, and the microscope can operate at magnifications that range from ~10 to 300,000. In addition to providing topographical information as in optical microscopes, it provides the information about chemical composition at the surface. In **SEM**, a source of electrons is concentrated into a beam, with a very fine spot size of **5-6 nm** and having energy in the range of a few hundred eV to 50 Kev that is rastered over the surface of the specimen with the help of deflection coils. A number of interactions occur between the surface and the e- beam as the beam strikes and penetrates the surface resulting in the emission of electrons (primary, secondary and backscattered) and photons. Images are produced from the cathode ray tube (CRT) by collecting the emitted electrons on it. The types of images produced in **SEM** are:

- Secondary (SE) electron images,
- Backscattered (BSE) electron images
- X-ray elemental maps.

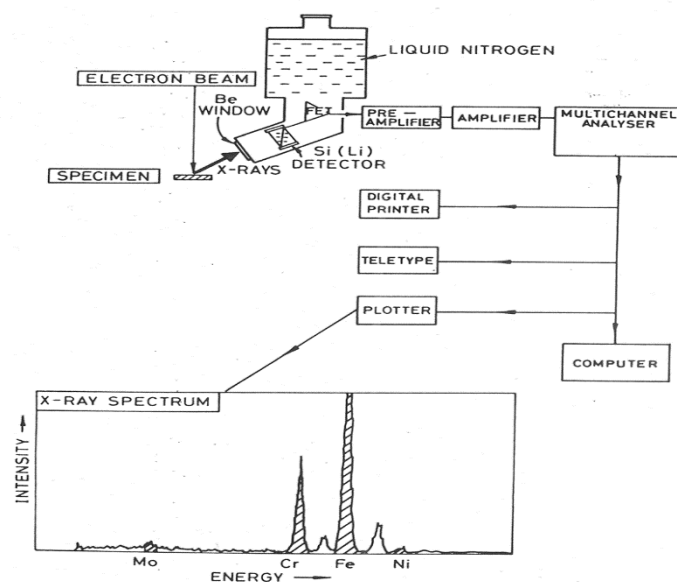




4.3.2 Energy Dispersive X-Ray Spectroscopy

X-rays enter energy dispersive spectrometer through a thin Be window and produce electron-hole pairs within the semiconductor crystal. Its mechanism includes a fast beam of electrons having high enough energy to excite all atoms in the periodic table. Then ionization of electrons from the K, L, or M shell. As a product of de-excitation we get x ray.

- Important uses
 - **Qualitative** use x-ray energy to identify elements
 - **Quantitative** use integrated peak intensity to determine amounts of elements



4.3.3 Differential Scanning Calorimetry:

Differential Scanning Calorimetry (DSC), is a type of thermal analysis technique that deals with the change of heat capacity (C_p) with change in temperature. Here both a sample substance and a reference substance are compared residing in separate chambers. The change in heat capacity as synonymous to change in heat flow is found out when a sample of known mass is heated or cooled. Examples of the types of data that can be inferred are; - glass transition temperature, melting temperature, phase change and curing temperature. As most of the materials show some kind of transition temperature DSC is used in many places due to its flexibility as in, polymers, paper, electronics, agriculture, food industry, paper industry semiconductors, and pharmaceuticals.

The advantages of DSC include versatility, ease of operation and faster operation and results to see different transition temperatures. The degree of purity of materials can be inferred from the phase changes occurring in liquid crystals, pharmaceuticals, metals and pure organics. If we are processing or distilling materials, knowledge of a material's enthalpy changes and heat capacity can be used to estimate how efficiently your process is operating. The efficiency of the process can be found out by knowing the materials heat capacity and enthalpy changes and comparing with the results. Due to this high efficiency DSC is used in most R and D laboratories all over the world.



Fig 3.2 Differential Scanning Calorimetry

4.3.4 Furnace

A furnace is an enclosed chamber used for heating via conduction, convection and radiation. The heat energy supplied to the furnace is in the form of fuel combustion, by electricity or through induction heating in induction furnaces. A muffle furnace (retort furnace) is a furnace in which the material is heated with stringent temperature conditions controlled with the help of a thermocouple. The heating soaking and cooling trends are achieved by manual operation of control panel

. Some of the advantages include

- Greater control of temperature
- Isolation of material being heated



4.3.5 X-ray Diffraction Analysis

XRD is one of the most important material characterization technique that has been used to find out parameters related to the crystal structure of solids, including lattice constants, spacing and geometrical packing, identification of unknown phases (intermetallics), orientation of single crystals and texture, preferred orientation of polycrystals, defects, Stresses, etc. In XRD, a collimated and concentrated beam of X-rays, interfere with the sample. There is a constructive interference of the incident ray with the diffracted ray according to Bragg's Law:

$$\lambda = 2d \sin \theta$$

Where

d = the spacing between consecutive atomic planes in the crystalline phase

λ = the wavelength of the beam.

The sample is scanned through 2θ angles, all possible patterns of diffraction are obtained. This graphical pattern is used to identify the peaks of intermetallics formation and specimen's crystalline phases. XRD is nondestructive and does not require elaborate sample preparation. It is because of this reason that XRD method is used in every materials characterization.

Uses

1) **Phase determination**

- Identification of crystalline phases

2) **Quantitative phase analysis**

- Relative composition of mixed phases

3) **Calculation of lattice parameters**

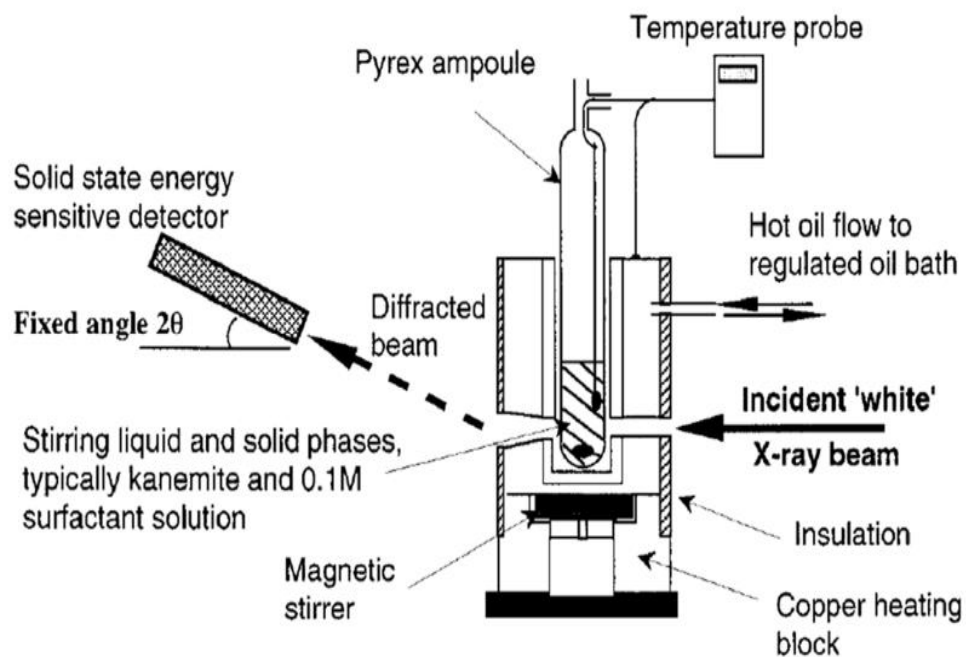
- Structural variations under different conditions

4) **Analysis of crystallite size and strain**

- Estimation of size of crystalline domain and disorder.

5) **Structure solution**

- Complete structure refinement of unknown phases.



5. RESULTS AND DISCUSSION

5.1 Microstructure of Zn-Sn-Al alloy solders

SEM analysis shows considerable heterogeneity of microstructure which will relate to the formation of non-equilibrium phases in the course of solidification. Mostly two or three types of phases of various chemical compositions were discovered, which was also proved by x ray microanalysis. The three phases were

White phase (C)- Contain high concentration of Tin without Aluminum

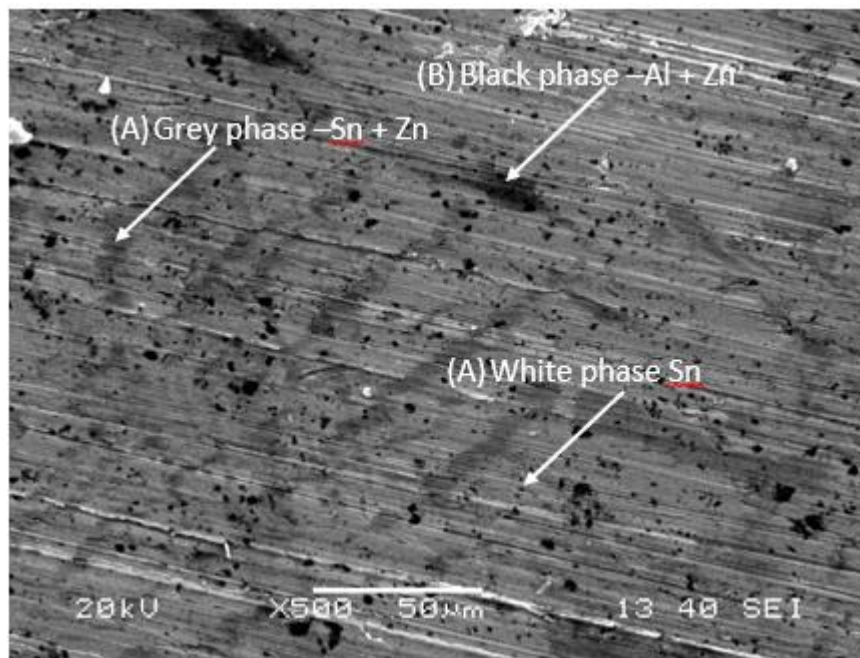
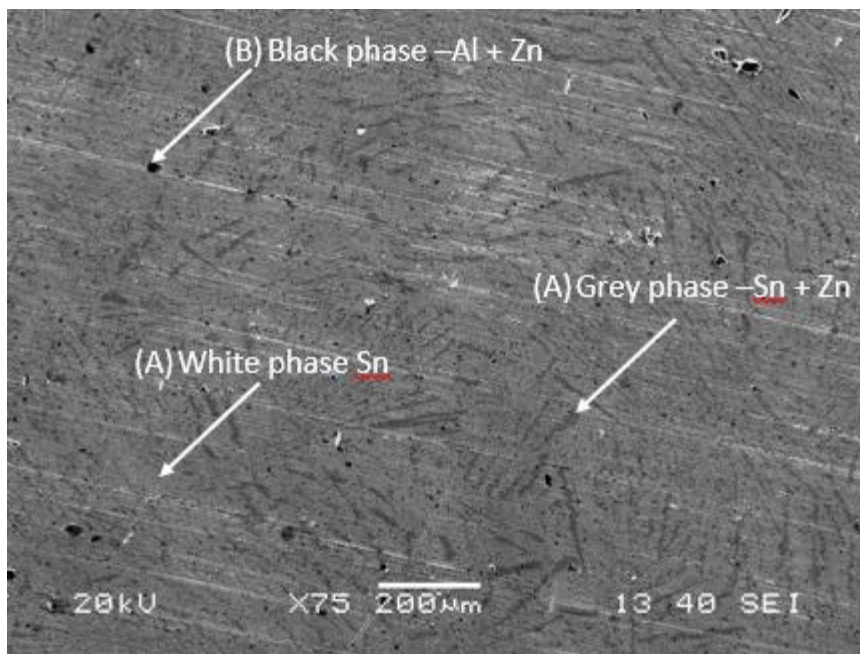
Grey phase (B) – Contain high concentration of Zinc without Tin.

Small Black phases (A)- Contain high concentration of Aluminum + Zinc and a certain concentration of Oxygen

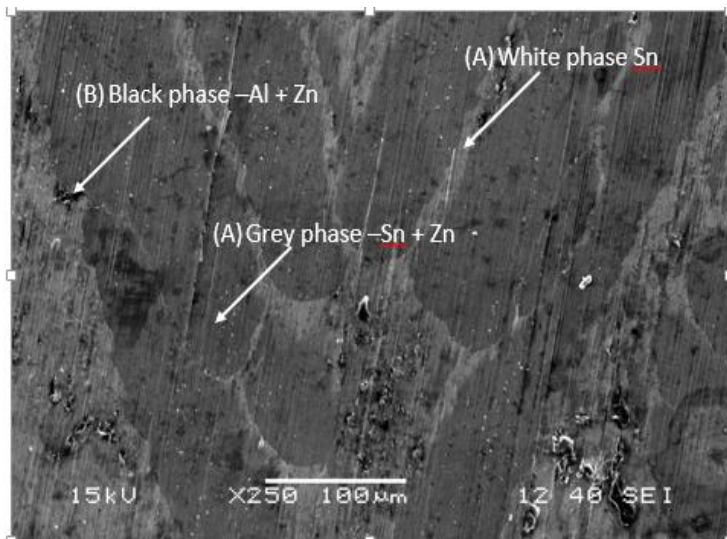
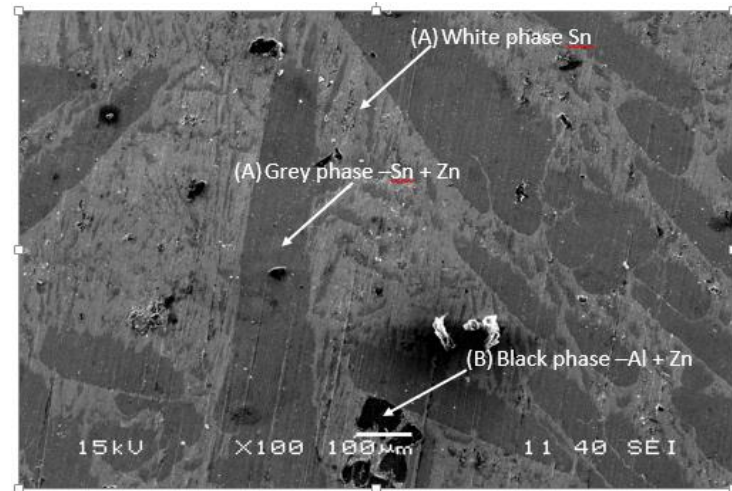
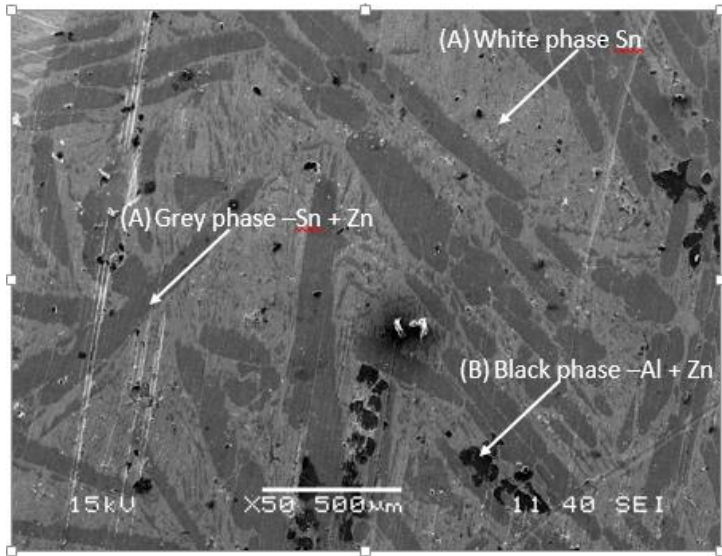
SEM image of Sample 1 and sample 3 consists of a eutectic lamellar structure while sample 2 consists of a dendritic structure. This is evident from the composition difference between the samples as the former being close to eutectic composition of binary Sn-Zn system. The three phases mentioned above are present in all three samples and are labelled as the primary and secondary precipitates A and B while the continuous matrix being labeled as C.

The primary precipitate A also known as ‘star shaped precipitates’ which forms first during solidification before eutectic reaction begins consists mainly Al+Zinc while the grey precipitate consists of Zinc mainly. The continuous matrix C which consists mainly of eutectic mixture of Sn and constitutes maximum of the volume fraction. The phase A accounting for the least volume percentage has a phase transition temperature higher than eutectic temperature in view of its high Al and Zn contents in comparing to that of the eutectic phase. The microstructure of air cooled sample is finer than the rest

SAMPLE 1 (3 Al- 15 Zn- 82 Sn –furnace cooled)

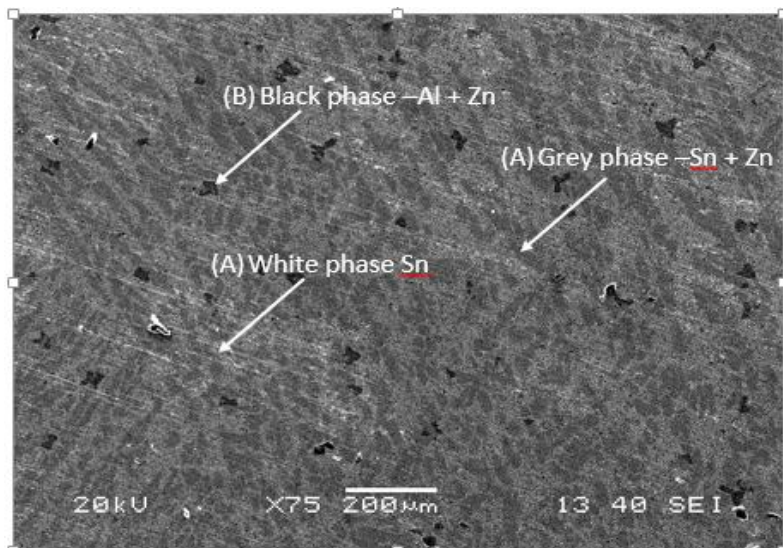
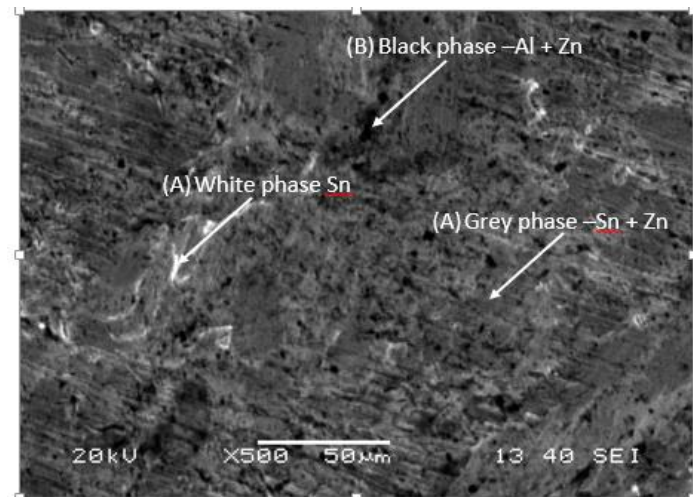
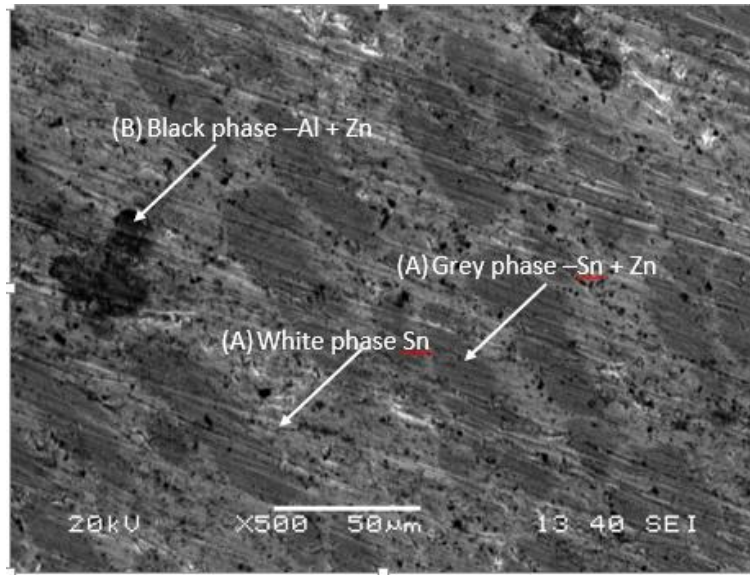


SAMPLE 2 (7 Al- 43 Zn- 50 Sn –furnace cooled)



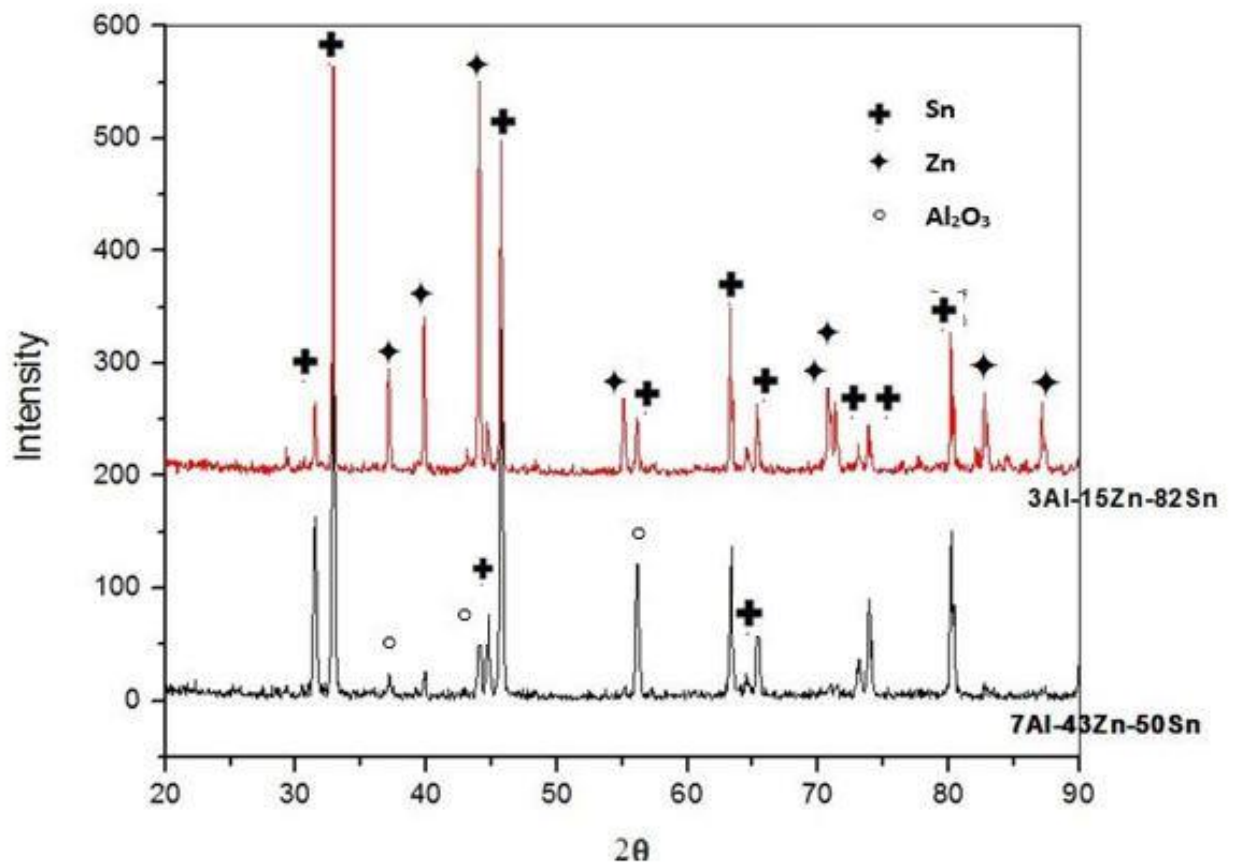
SAMPLE 3 (3 Al- 15 Zn- 82 Sn –air cooled)

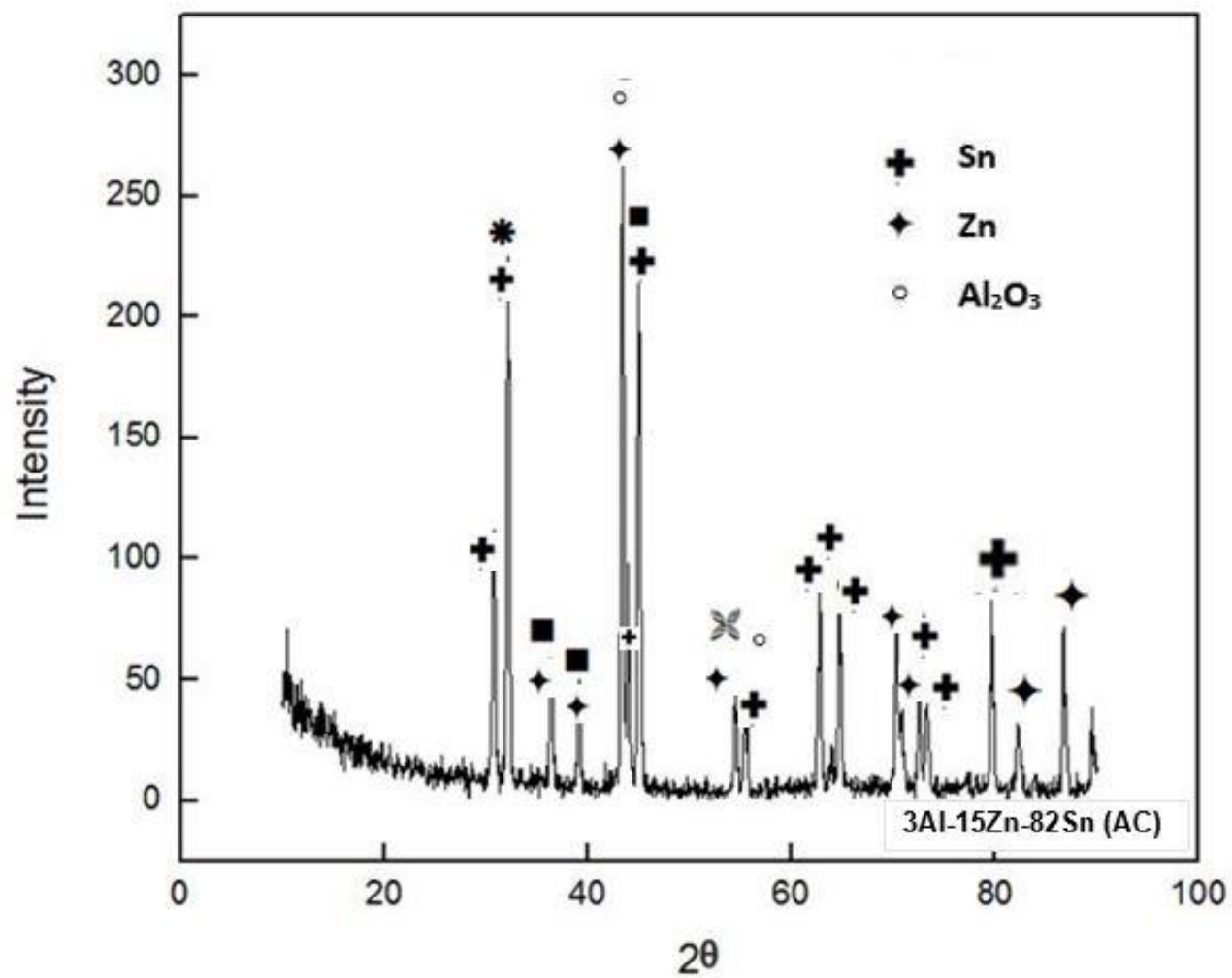
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5.2 XRD ANALYSIS

The XRD plots of the three samples prepared are shown in figures. The phases present in these samples are shown and labeled. From these phases we can see that considerable oxidized phases is present which is Al_2O_3 . The highest peak of Sn is presented by the peak $2\theta = 33, 46$ degrees. Other elemental peaks of Zn are also prominent at $2\theta = 40, 45$ degrees. The absence of ZnO peaks is suggestive of preferential oxidation of Aluminum over Zinc





5.3 Thermal Analysis of Zn- Sn – Al Alloy solder

The melting temperature (T_m) is quite an important physical property and has a great effect on printed circuit board (PCB) assembly. A good Solder alloy must have a lower melting temperature. Figure below shows the DSC curve of Sample 3Al-15Zn-82Sn (Furnace Cooled) upon heating at a scanning rate of 10°C/min .

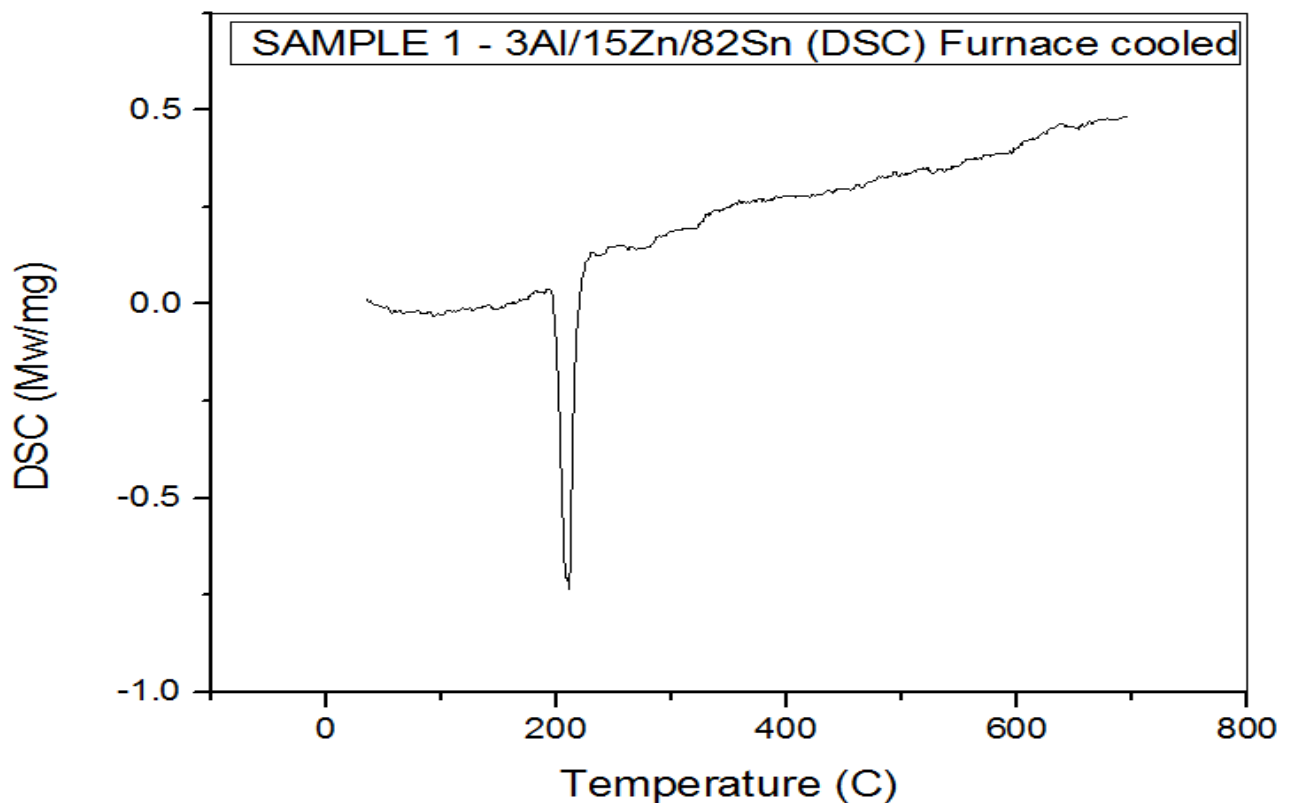


Figure below shows the DSC curve of Sample 7Al-43Zn-50Sn (Furnace Cooled) upon heating at a scanning rate of 10°C/min .

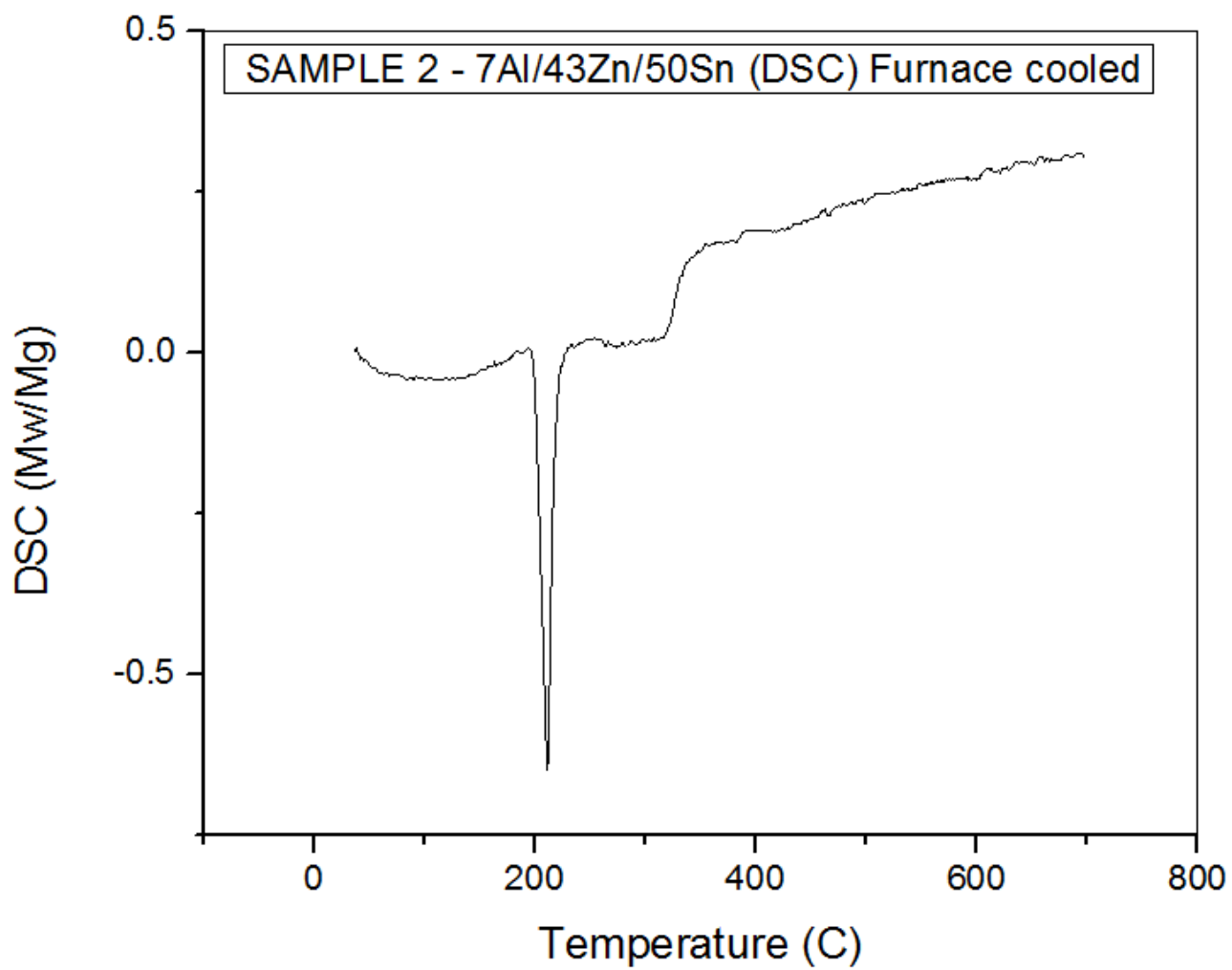
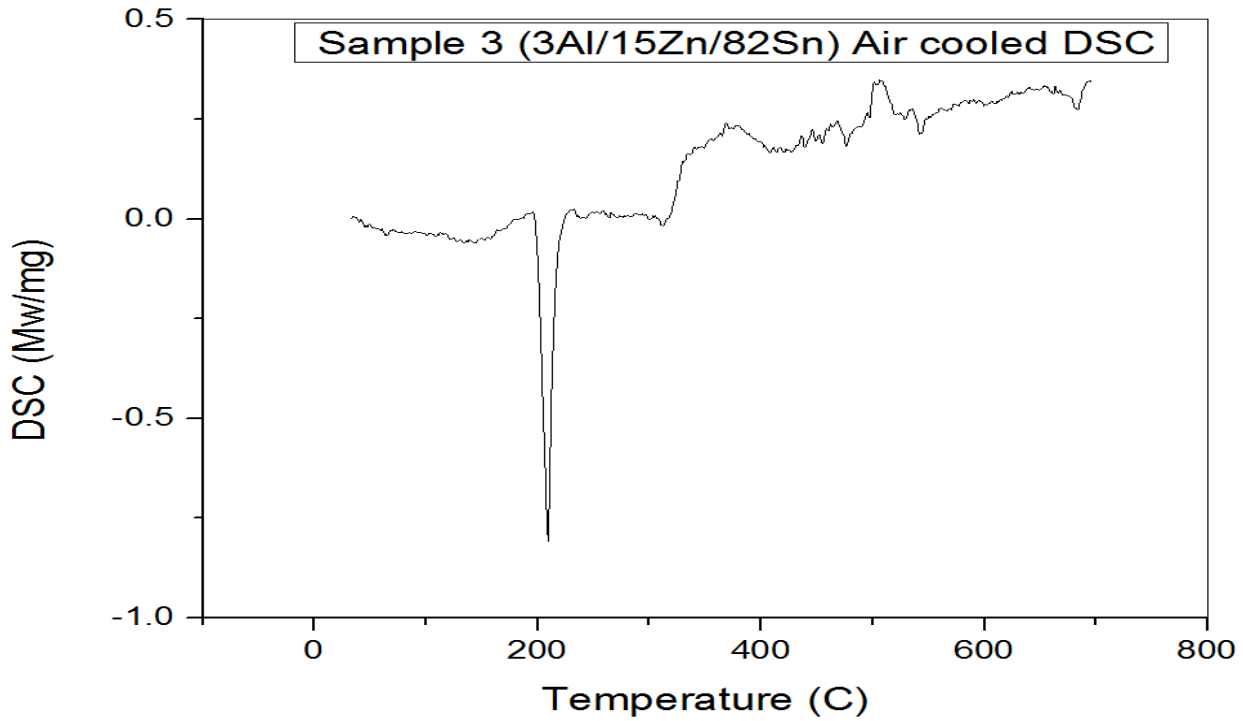
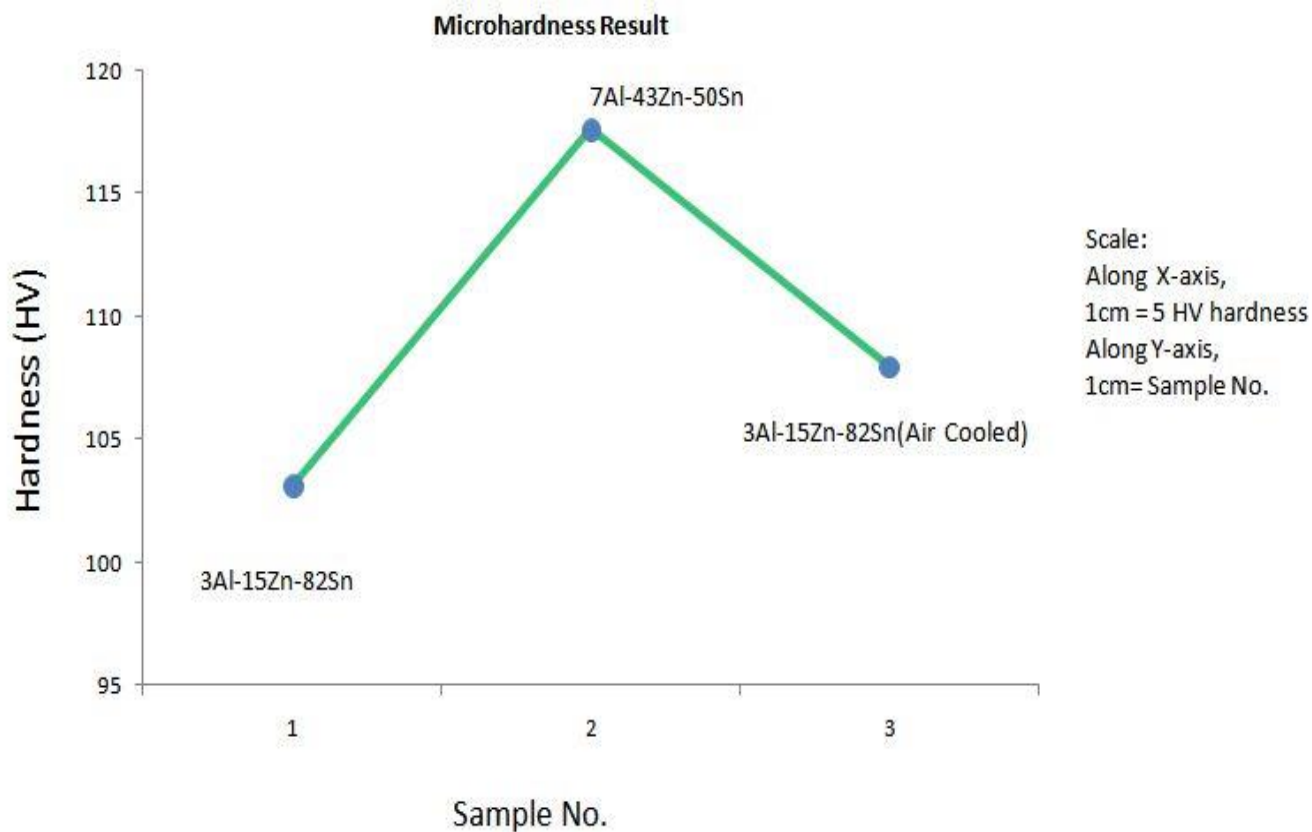


Figure below shows the DSC curve of Sample 3Al-15Zn-82Sn (Air Cooled) upon heating at a scanning rate of 10° C/min.



DSC result shows an endothermic peak at 210.9 ° C, 211.3° C and 209.5 ° C for 3Al-15Zn-82Sn (Furnace Cooled), 7Al-43Zn-50Sn (Furnace Cooled) and 3Al-15Zn-82Sn (Air Cooled) Samples respectively. This data correspond to the melting temperature of Sn-8.8Zn eutectic composition (198 ° C). Hence, it is confirmed that a eutectic alloy has been formed in all the three cases. The difference in the melting temperatures can be attributed to the oxide formation. The oxygen may be absorbed by the specimen's surface during the process of melting, grinding and polishing.

5.4 Micro hardness



Vickers Micro-hardness test was performed on the prepared samples. It was concluded that 7Al-43Zn-50Sn had the highest value of hardness among the three samples. Also, 3Al-15Zn-82Sn (Air Cooled) sample had a greater value of hardness than 3Al-15Zn-82Sn (Furnace Cooled). The reason can be attributed to the higher rate of cooling while cooling in the presence of air which leads to finer microstructure. It has also been observed that the micro-hardness value decreases with the increase in the tin content and Aluminum increases the micro-hardness specifically with higher Zinc contents. Tin, as an element, has a lower hardness than Zinc.

Elements	Mohs Hardness	Brinell Hardness(GPa)
Tin	1.5	0.0051
Zinc	2.5	0.412
Aluminum	3	0.245

Constant load =25gf

Sample 1(3Al-15Zn-82Sn (Furnace Cooled))

Diagonal 1(μm)	Diagonal 2(μm)	Micro-Hardness Value(HV)
22.42	22.42	92.9
22.46	19.19	106.9
24.32	25.21	75.6
19.92	16.89	136.9

The average hardness for sample 1 is **103.075HV**

Sample 2(7Al-43Zn-50Sn (Furnace Cooled))

Diagonal 1 (μm)	Diagonal 2(μm)	Micro-Hardness Value(HV)
20.32	21.01	108.6
17.5	18.1	148.2
22.08	22.42	93.6
19.99	19.19	120.1

The average hardness for sample 2 is **117.625HV**

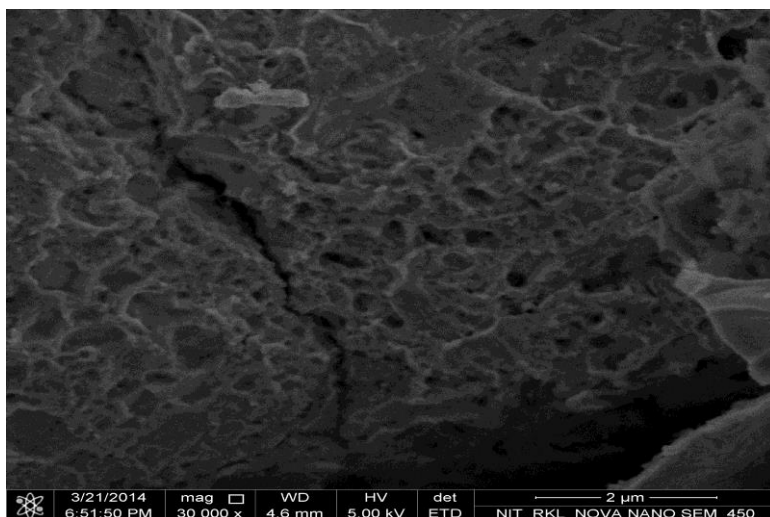
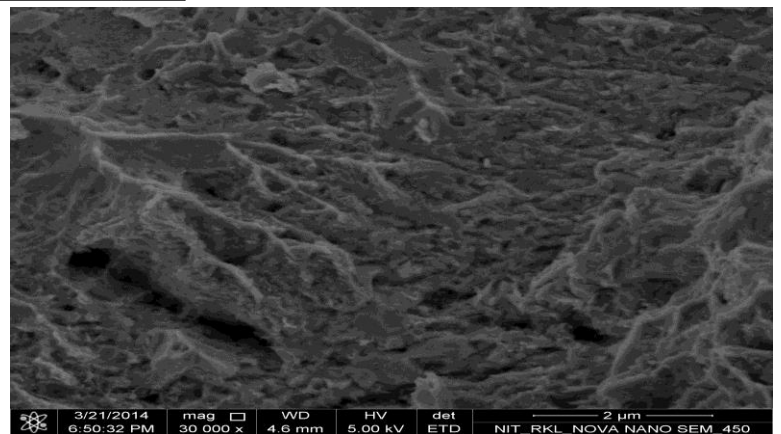
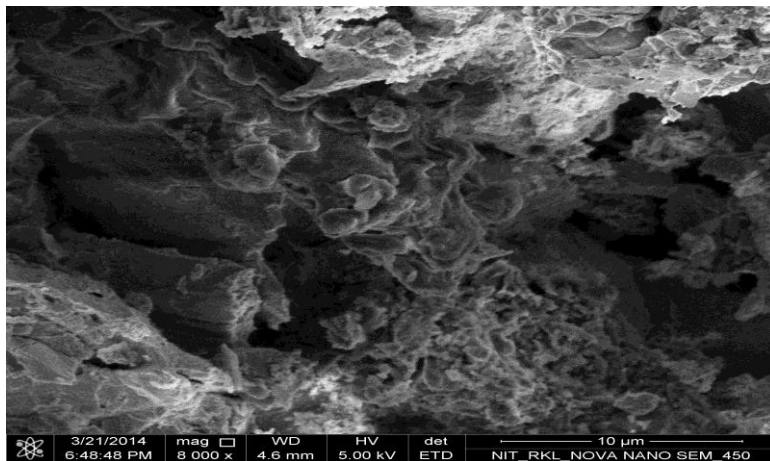
Sample 3(3Al-15Zn-82Sn (Air Cooled))

Diagonal 1(μm)	Diagonal 2(μm)	Micro-Hardness Value(HV)
17.5	18.6	142.1
20.9	21.6	102.4
22.42	21.6	94.7
22.52	22.41	92.6

The average hardness for sample 3 is **107.95HV**

5.5 Fracture analysis

The fracture surface of the solder alloy was analyzed using FESEM (Field Emission Scanning Electron Microscopy). The fracture surface of the alloys show dimpled structure which indicate that there is ductile nature of fracture. There are no flat smooth fracture surface to prove brittle fracture. This indicates that due to presence of high Sn we get ductile failure.



CONCLUSIONS

- ✓ The three different solders of above compositions were successfully developed.
- ✓ The melting point of sample 1, 2 and 3 were 210.9, 211.3 and 209.5 °C respectively. It is higher by an amount of 10-12 degrees than the eutectic temperature of Sn-Zn eutectic temperature (198 °C). This change of temperature is attributed to addition of Al and deviation from eutectic composition. This change is welcomed as not only we get a lead free alloy but also we reduce the oxidation and corrosion of Zn by the atmosphere.
- ✓ By XRD plot we see that there is no prominent peak of ZnO but there are few peaks of Al₂O₃. This illustrated the preferential oxidation of Al rather than Zn which is also depicted by the corresponding lines in the Ellingham diagram. SnO is not formed as Sn is very hard to oxidize even at higher temperature.
- ✓ The hardness increases as we add more Zn as is depicted by the micro hardness graph. Air cooling gives a finer microstructure (size of grey phase) which results in high hardness values.
- ✓ The fracture surface of the solder indicates that there is ductile fracture owing to presence of dimples in the structure.

REFERENCES

- [1] Massalski T.B., Okamoto H. Binary Alloy Phase Diagrams. American Society for Metals, Metals Park, Ohio, 1996,
- [2] Dorward R.C. Metal Trans., 7A, 1976, No. 2, p. 308-310.
- [3] Prowans S., Bohatyrewicz M. Układ aluminium – cyna – cynk. Arch. hutn., 13, 1968, No. 2. p. 217-233.
- [4] Nayak A.K. Trans. Indian Inst. Met., 28, 1975, No. 2, p. 285-290
- [5]. P.T. Vianco and D.R. Frear, *JOM* 45 (7), 14 (1993).
- [6]. J.W. Morris, Jr., J.L. Freer Goldstein and Z. Mei, *JOM* 45 (7), 25 (1993).
- [7]. C.H. Raeder, L.E. Felton, V.A. Tanzi and D.B. Knorr, *J. Electron. Mater.* 23, (7), 611 (1994).
- [8]. L.E. Felton, C.H. Raeder and D.B. Knorr, *JOM* 45 (7), 28(1993).
- [9]. M. McCormack, S. Jin, H.S. Chen and D.A. Machusak, *J. Electron. Mater.* 23, (7), 687 (1994).
- [10]. M. McCormack and S. Jin, *J. Electron. Mater.* 23 (7), 635(1994).